[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. III. Nuclear Substitutions

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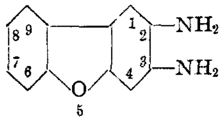
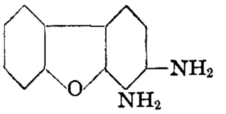
Introduction

Homonuclear Substitution.—It is reasonable to predict that a uni-nuclear substituted dibenzofuran containing a substituent which in benzene is a strong *o,p*-director will orient a second substituent predominantly to the same nucleus. This is generally the case, but the exact position assumed by the second substituent is frequently uncertain. Nitration of 3-diacetaminodibenzofuran, followed by hydrolysis and then reduction of the nitro group, gives a diamine which must have the amino groups *ortho* to each other because it yields quinoxaline derivatives.[1]

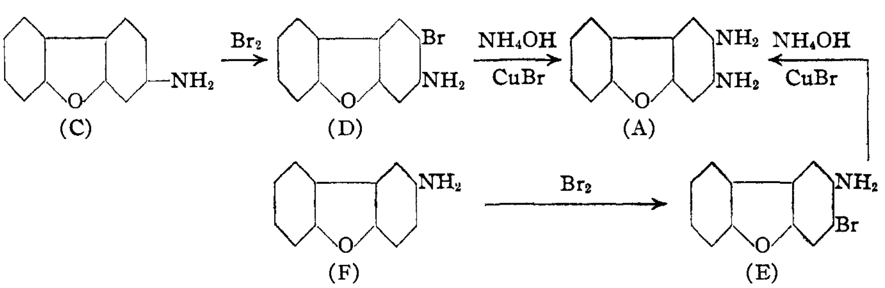


(A)



(B)

Formula (A) was suggested, and unpublished studies by Brumberg confirmed this structure by first replacing the amino group of the nitro-3-aminodibenzofuran by hydrogen (*via* diazotization), and then successively reducing the nitro group to an amine, diazotizing, replacing the diazonium group by a cyano group and hydrolyzing to give the known 2-dibenzofurancarboxylic acid. Borsche and Schacke[2] had suggested that possibly this 2-nitrodibenzofuran (obtained subsequent to nitration of 3-aminodibenzofuran) was identical with a supposed 4-nitrodibenzofuran formed in small quantities by nitration of dibenzofuran. Accordingly, Cullinane[3] postulated that the diamine from nitro-3-aminodibenzofuran might be 3,4-diaminodibenzofuran (B) on the basis of a synthesis of 2-nitrodibenzofuran[4] which showed this compound to be unlike the supposed 4-nitrodibenzofuran.



The confusion is attributable to two things. First, there is no unequivocal evidence, at this time, for the existence of a 4-nitrodibenzofuran, and the compound so designated is almost certainly a mixture of nitrodibenzofurans, formed incidental to 3-nitrodibenzofuran which is the chief product of nitration of dibenzofuran. Second, the results described in the thesis by Brumberg are relatively, and understandingly, unknown. We have shown that the 3-amino group orients a second substituent to the 2-position. This was proved by starting with a 2-substituted dibenzofuran and establishing the identity of the *ortho*-di-substituted dibenzofuran so obtained with that derived from a 3-substituted dibenzofuran.

In addition, 2-bromo-3-aminodibenzofuran (D) was converted to the known 2-bromodibenzofuran, by means of the diazo reaction; and, in like manner, 2-amino-3-bromodibenzofuran (E) gave the known 3-bromodibenzofuran.

Nitration of the 2-amino (F) and 3-amino (C) compounds proceeded as in bromination, the nitro group going, respectively, to the 3- and to the 2-positions. A mixed melting point determination with Brumberg's 2-acetamino-3-nitrodibenzofuran, kindly provided by Professor Borsche, established the identity of our compound. Bromination and nitration were effected with the acetamino compounds and not with the free amines. We have observed, however, that by starting with 3-diacetaminodibenzofuran the disubstitution product is a *mono*-acetamino compound,[2] which is in agreement with substitution reactions of 2-diacetaminodibenzofuran.[1] Furthermore, we have found that 3-acetaminodibenzofuran does undergo nitration and the use of 3-diacetaminodibenzofuran is not necessary.[2]

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(1) F. Brumberg, Doctoral Dissertation, Göttingen, 1925.

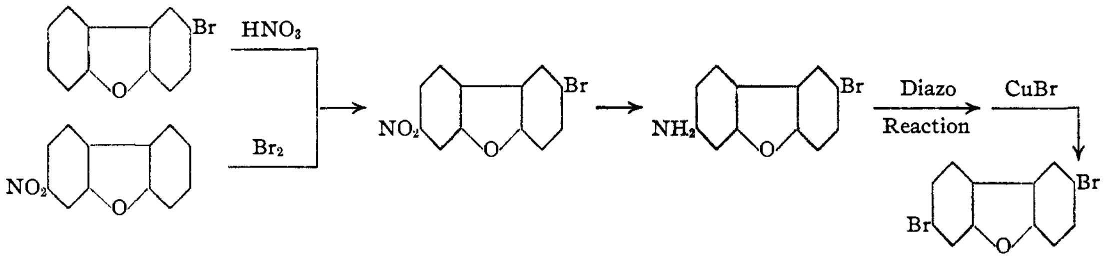
(2) Borsche and Schacke, *Ber.*, **56**, 2504 (1923).

(3) Cullinane, *J. Chem. Soc.*, 2267 (1930).

(4) Ryan, Keane and McGahon, *Proc. Roy. Irish Acad.*, **37B**, 368 (1927); [*C. A.*, **22**, 70 (1928)].

Heteronuclear Substitution.—The only evidence now available on heteronuclear disubstitution reactions is concerned with the introduction of like substituents. With nitration, the product is 2,7-dinitrodibenzofuran;[5] with sulfonation, 2,8-dibenzofurandisulfonic acid;[6] and with bromination, 2,8-dibromodibenzofuran.[7] Dichlorination gave as the predominant product 2,8-dichlorodibenzofuran, which was shown to be identical with an authentic specimen (prepared by ring closure)[7] kindly provided by Professor McCombie. Likewise, di-iodination gave 2,8-di-iododibenzofuran, the constitution of which was established by showing the compound to be the same as that obtained by treating 2,8-dichloromercuridibenzofuran[6] with iodine.

Nitration of 2-bromodibenzofuran has been reported to yield a mixture of isomers, which was not resolved; and, on the basis of an unsuccessful attempt to replace the bromine by an amino group, by the use of alcoholic ammonium hydroxide, it was concluded that no 2-bromo-3-nitrodibenzofuran was contained in the mixture.[1] More recently,[8] it has been demonstrated that bromination of 3-nitrodibenzofuran and nitration of 2-bromodibenzofuran yielded the same compound. The formula assigned to this compound, without experimental proof, is 2-bromo-7-nitrodibenzofuran. We have obtained the same product by these two substitution reactions, and have shown it to be the suggested 2-bromo-7-nitrodibenzofuran by the following sequence of reactions.



The 2,7-dibromodibenzofuran obtained in this manner was shown to be identical with an authentic specimen prepared by ring closure.[7,9] Confirmatory evidence for the correctness of the nitro-bromo structure was secured by converting the compound, by two different series of reactions, to the known 2,7-diaminodibenzofuran (see Experimental Part).

In addition to the 2-bromo-7-nitrodibenzofuran from nitration of 2-bromodibenzofuran, we obtained an isomeric 2-bromo-3-nitrodibenzofuran. The structure of this compound was established by reducing it to the previously mentioned 2-bromo-3-aminodibenzofuran (D).

Mechanism of Nuclear Substitution.—Dibenzofuran is peculiarly adapted to throw light on some possible mechanisms of nuclear substitution. The position assumed by a nuclear substituent with dibenzofuran appears to depend markedly on the nature of the substituent: for example, halogenation and sulfonation involve the 2-position; nitration, the 3-position; and metalation,[10] the 4-position. In iodination by means of iodine and mercuric oxide there is the possibility that mercuration is the first reaction and that subsequently the mercuri group is replaced by iodine. A sequence of reactions of this kind is rendered highly remote, for mercuration takes place in the 4-position,[10] and the iodo compound actually isolated by Mr. R. V. Young was 2-iodidibenzofuran. In iodination by iodine and nitric acid, the possibility of preliminary nitration followed by replacement of the nitro group by iodine is excluded in the case of dibenzofuran, for otherwise a 3- and not the observed 2-iododibenzofuran would have formed.

Experimental Part

Bromination of 3-Acetaminodibenzofuran.—To a solution of 10 g. (0.044 mole) of 3-monoacetaminodibenzofuran (prepared in accordance with the directions of Borsche and Schacke[3]) in 75 cc. of glacial acetic acid was added dropwise 7 g. (0.044 mole) of bromine. The bromo compound which separated was filtered, washed with water and crystallized from alcohol to give an 85% yield of product melting at 192°. Recrystallization of the 2-bromo-3-acetaminodibenzofuran raises the melting point to 194°.

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(5) Cullinane, *J. Chem. Soc.*, 2365 (1932).

(6) Gilman, Smith and Oatfield, THIS JOURNAL, **56**, 1412 (1934).

(7) McCombie, Macmillan and Scarborough, *J. Chem. Soc.*, 535 (1931).

(8) Cullinane, Davey and Padfield, *ibid.*, 716 (1934).

(9) The authors are grateful to Professor McCombie for the specimen of this compound which was used in a mixed melting point determination.

(10) Gilman and Young, THIS JOURNAL, **56**, 1415 (1934).

Anal. Calcd. for $C_{14}H_{10}O_2NBr$: N, 4.60. Found: N, 4.76 and 4.89.

3-Diacetaminodibenzofuran, prepared after the directions of Borsche and Bothe,[11] was brominated in like manner to give an 80% yield of the same 2-bromo-3-acetaminodibenzofuran.

The bromoacetamino compound (7 g.) was hydrolyzed by refluxing for one hour with 25 cc. of concd. hydrochloric acid in 75 cc. of alcohol to give the hydrochloride, which is slightly soluble in water and decomposes at 236°. The 2-bromo-3-aminodibenzofuran was obtained quantitatively by adding an excess of ammonium hydroxide to a suspension of the hydrochloride in water, and melted at 129° after recrystallizing from alcohol.

Anal. Calcd. for $C_{12}H_8ONBr$: N, 5.34. Found: N, 5.40.

2-Bromo-3-aminodibenzofuran (D) was diazotized, and the diazonium group was replaced by hydrogen by means of alcohol, to give 2-bromodibenzofuran (mixed melting point).

The 2-bromo-3-aminodibenzofuran (3 g. or 0.011 mole) was converted to 2,3-diaminodibenzofuran (A) by heating in a sealed tube at 190° for twenty hours with 40 cc. of ammonium hydroxide and 2 g. of cuprous bromide. The diamine melted at 165–166°, after crystallization from an aqueous alcohol solution, and darkened on atmospheric exposure. It was shown to be identical with the diamine of Borsche and Schacke,[2] the quinoxaline derivatives with benzil and phenanthraquinone melting at 179 and 297°, respectively.

Nitration of 3-Acetaminodibenzofuran.—The first series of nitration reactions was carried out with 3-diacetaminodibenzofuran, and involved nitration, de-acetylation to 2-nitro-3-aminodibenzofuran, reduction to 2,3-diaminodibenzofuran, and characterization of the diamine by formation of the quinoxaline derivatives with benzil and phenanthraquinone. In this sequence of reactions, the melting points of our several compounds agreed with those reported by Borsche and Schacke.[2] However, their supposed 2-nitro-3-diacetaminodibenzofuran is in reality 2-nitro-3-acetaminodibenzofuran.

3-Acetaminodibenzofuran (10 g. or 0.044 mole) in acetic acid was nitrated to give a 75% yield of 2-nitro-3-acetaminodibenzofuran, melting at 196° after recrystallization from acetic acid, and identical with the supposed 2-nitro-3-diacetaminodibenzofuran.

Anal. Calcd. for $C_{14}H_{10}O_4N_2$: N, 10.37. Found: N, 10.02 and 10.42.

2-Nitro-3-acetaminodibenzofuran (5.4 g. or 0.02 mole) was suspended in a solution of 25 cc. of concd. hydrochloric acid with 75 cc. of alcohol and diazotized; the diazo solution was heated to replace the diazo group by hydrogen; and the product, isolated in 40% yield, was 2-nitrodibenzofuran which melted at 149° after crystallization from alcohol. The nitro compound was shown to be identical with a sample of Brumberg's 2-nitrodibenzofuran, prepared by the same series of reactions, and kindly provided by Professor Borsche.

Anal. Calcd. for $C_{12}H_7O_3N$: N, 6.57. Found: N, 6.64 and 6.79.

The 2-nitrodibenzofuran was reduced by tin and hydrochloric acid to 2-aminodibenzofuran, melting at 125–126° and identical with the amine obtained by amination of 2-bromodibenzofuran. To further establish the correctness of the structure of the 2-aminodibenzofuran, the compound was diazotized and the diazo group replaced by chlorine to give 2-chlorodibenzofuran melting at 102°. The 2-chlorodibenzofuran was shown to be identical with an authentic specimen prepared by ring closure.

Bromination of 2-Diacetaminodibenzofuran.—The necessary 2-aminodibenzofuran was prepared by amination of 2-bromodibenzofuran which was synthesized in accordance with the directions of Mayer and Krieger.[12] The yield of 2-bromodibenzofuran, starting with technical dibenzofuran, was 62% and significant losses were noted when purification was effected either by crystallization from toluene or distillation under reduced pressure.

The 2-bromodibenzofuran (48 g. or 0.153 mole) was converted to the hydrochloride of 2-aminodibenzofuran by heating in a steel bomb at 200–210° for ten hours with 35 g. of cuprous chloride and 500 cc. of ammonium hydroxide (sp. gr., 0.89). The yield was 30 g. or 88.7%. In other preparations carried out at different temperatures and varying times of heating the yields were 74.6 and 82%. Smaller quantities of the amine hydrochloride can be prepared under corresponding conditions by heating in a sealed tube, and the yield of crude amine hydrochloride starting with 1.5 g. of 2-bromodibenzofuran was 81%. The position of the amino group was established by diazotization, either in the usual manner or in accordance with the procedure described recently by Schoutissen,[13] and subsequent replacement of the diazo group by bromine to yield 2-bromodibenzofuran.

2-Diacetaminodibenzofuran was prepared in 70% yields by heating 25 g. (0.113 mole) of 2-aminodibenzofuran hydrochloride for one hour with 125 cc. of acetic anhydride, 20 cc. of acetic acid and 25 g. of anhydrous sodium acetate.

A solution of 15 g. (0.056 mole) of 2-diacetaminodibenzofuran in acetic acid was brominated by an equivalent quantity of bromine to give a 41% yield of crude 2-acetamino-3-bromodibenzofuran melting at 203–216°. Recrystallization from 90% acetic acid raised the melting point to 240–241°.

Anal. Calcd. for $C_{14}H_{10}O_2NBr$: N, 4.60. Found: N, 4.67 and 5.05.

The mother liquors yielded material melting between 186–195° after crystallization from aqueous alcohol. It is probable that isomers are formed in the bromination.

The 2-acetamino-3-bromodibenzofuran was hydrolyzed by alcoholic hydrochloric acid to give an amine hydrochloride which with ammonium hydroxide yielded 2-amino-3-bromodibenzofuran (E) in quantitative yield. The bromo-amine after recrystallization from alcohol melted at 172–173°.

Anal. Calcd. for $C_{12}H_8ONBr$: N, 5.34. Found: N, 5.45 and 5.64.

2-Amino-3-bromodibenzofuran (1 g.) was aminated by heating in a sealed tube with cuprous chloride and ammo-

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[11] Borsche and Bothe, *Ber.*, **41**, 1940 (1908).

[12] Mayer and Krieger, *Ber.*, **55**, 1659 (1922). A synthesis of 2-aminodibenzofuran from 2-bromodibenzofuran has just been described, German Patent 591,213 [*C. A.*, **28**, 2366 (1934)].

[13] Schoutissen, THIS JOURNAL, **55**, 4532 (1933).

nium hydroxide at 165–175° for two hours and then at 215° for eight hours. The quinoxaline derivative prepared from this diamine and benzil melted at 184–185° after thrice recrystallizing from alcohol. The mixed melting point with the corresponding quinoxaline (m. p. 178.5–179.5°) prepared from 2-bromo-3-aminodibenzofuran was 178.5–181.5°.

2-Amino-3-bromodibenzofuran was converted in 80% yield to 3-bromodibenzofuran[14] by means of the diazo reaction.

Nitration of 2-Diacetaminodibenzofuran.—Nitration of 2-diacetaminodibenzofuran in acetic acid by fuming nitric acid gave 2-acetamino-3-nitrodibenzofuran, identical with a sample of Brumberg's[1] compound. From the dilute acetic acid mother liquors there was obtained a compound which when recrystallized from 90% alcohol melted at 161.5–162.5°, and when hydrolyzed gave a small quantity of 2-aminodibenzofuran.

Anal. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: N, 6.18 and 6.21.

This compound melting at 161.5–162.5° is very probably 2-acetaminodibenzofuran, for a mixed melting point with the acetylation product of 2-aminodibenzofuran showed no depression.

The 2-acetamino-3-nitrodibenzofuran was first hydrolyzed to the nitro-amine and this was then reduced to the 2,3-diaminodibenzofuran, by tin and hydrochloric acid. The diamine melted at 164–166° after recrystallization from aqueous alcohol. The quinoxaline derivative prepared by interaction with benzil melted at 184–185° as was the case with the quinoxaline synthesized from the diamine obtained from 2-amino-3-bromodibenzofuran. The mixed melting point with the corresponding quinoxaline (m. p. 178.5–179.5°) obtained through 2-bromo-3-aminodibenzofuran was again 178.5–181.5°. It appears rather certain that the quinoxaline derived from 2-amino-3-bromodibenzofuran and 2-amino-3-nitrodibenzofuran is purer than that reported previously. Also, both 2-amino-3-bromo (or 3-nitro)-dibenzofuran and 2-bromo (or 2-nitro)-3-aminodibenzofuran yield the same 2,3-diaminodibenzofuran, for the diamine from 2-amino-3-nitrobenzofuran gives a quinoxaline with phenanthraquinone the melting point of which alone and when admixed with the corresponding quinoxaline from 2-bromo (or 2-nitro)-3-aminodibenzofuran is 302–303°.

It is significant that neither nitration nor bromination of the acetylated 2-aminodibenzofuran gives a 1-substituted product. Some stereochemical aspects of dibenzofuran will be considered in forthcoming articles.

2,8-Dichlorodibenzofuran.—Chlorine gas was passed into a stirred solution of 84 g. (0.5 mole) of dibenzofuran in 300 cc. of carbon tetrachloride to the formation of a heavy precipitate. The temperature of the mixture rose rapidly to 40°, and was maintained at that point. The 2,8-dichlorodibenzofuran (38% yield) melted at 185° after first crystallizing from ethyl alcohol and then from chloroform, and showed no depression with a specimen prepared by ring closure.

Anal. Calcd. for $C_{12}H_6OCl_2$: Cl, 29.92. Found: Cl, 30.05 and 30.45.

The addition of 0.5 mole of chlorine to a stirred solution of 84 g. (0.5 mole) of dibenzofuran in 350 cc. of glacial acetic acid at a temperature of 60° gave 16.3 g. of 2-chlorodibenzofuran melting at 102.5° and showing no depression in a mixed melting point determination with a sample prepared by ring closure.[7]

Anal. Calcd. for $C_{12}H_7OCl$: Cl, 17.51. Found: Cl, 17.65, 17.83 and 17.78.

The same 2-chlorodibenzofuran (mixed melting point) was obtained by heating dibenzofuran with phosphorus pentachloride.[15]

2-Iodobenzofuran and 2,8-Di-iododibenzofuran.—2-Iododibenzofuran was obtained in 45% yield by stirring vigorously a solution of 16.8 g. (0.1 mole) of dibenzofuran, 12.7 g. (0.1 mole) of iodine and 7 cc. of concd. nitric acid in 100 cc. of chloroform, the mixture being refluxed for four hours. The iodo compound melts at 112°, and crystallizes in large leaves from alcohol.

Anal. Calcd. for $C_{12}H_7OI$: I, 43.2. Found: I, 43.8 and 43.65.

The 2-iododibenzofuran readily forms the corresponding Grignard reagent which gives a positive color test,[16] and on carbonation yields 2-dibenzofurancarboxylic acid.

2,8-Di-iododibenzofuran was secured in a 47% yield by adding 60 cc. of concd. nitric acid to a solution made up of 33.2 g. (0.2 mole) of dibenzofuran and 48.4 g. (0.4 mole) of iodine in 150 cc. of chloroform. The mixture was refluxed and stirred for two hours, at the end of which time the free iodine color was discharged and precipitation set in. The di-iodo compound crystallizes from chloroform in long, pale yellow needles melting at 173°. It was shown to be identical with the di-iodo compound prepared from 2,8-dichloromercuridibenzofuran.

Anal. Calcd. $C_{12}H_6OI_2$: I, 60.46. Found: I, 60.61 and 60.76.

The product from the mother liquors after crystallizing from chloroform consisted chiefly of 2-iododibenzofuran.

2-Bromo-7-nitrodibenzofuran. (A) **from 2-Bromodibenzofuran.**—To a solution of 49.4 g. (0.2 mole) of 2-bromodibenzofuran in 175 cc. of acetic acid was added 40 cc. of fuming nitric acid (sp. gr. 1.52). The mixture was heated at 70–75° for one-half hour, at the end of which time a pale yellow precipitate started to separate. The crude yellow product, after washing with water to free of acids, weighed 48 g. and melted between 136–200°. From the material insoluble in hot benzene there was obtained a 25% yield of 2-bromo-7-nitrodibenzofuran. The melting point after crystallization from a large volume of acetone is 250.5–251.5°.

Anal. Calcd. for $C_{12}H_6O_3NBr$: Br, 27.37. Found: Br, 27.12 and 27.09.

(B) From 3-Nitrodibenzofuran.—Bromine (9.6 g. or 0.06 mole) was added slowly to a stirred suspension of 10 g. (0.047 mole) of 3-nitrodibenzofuran in 75 cc. of acetic acid heated to 70°. After an additional four-hour period of heating at 65–70°, the mixture was cooled and the filtered product washed with water, and fractionally crystallized from glacial acetic acid to give a 14% yield of 2-

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(14) Prepared by Paul T. Parker from 3-aminodibenzofuran by diazotization.

(15) Hoffmeister, *Ber.*, **3**, 757 (1870); *Ann.*, **159**, 211 (1871); Whitmore and Langlois, This Journal, **55**, 1518 (1933).

(16) *Ibid.*, **47**, 2002 (1925).

bromo-7-nitrodibenzofuran. The acetic acid liquors gave a fraction melting between 169–183°; this was not investigated.

Reduction of 2-Bromo-7-nitrodibenzofuran.—Reduction of the nitro group was effected both by zinc and alcoholic hydrochloric acid (33% yield) and by tin and concd. hydrochloric acid (56% yield). 2-Bromo-7-aminodibenzofuran, liberated from the amine hydrochloride, by ammonium hydroxide, melted at 133–134° after crystallization from alcohol.

Anal. Calcd. for $C_{12}H_8ONBr$: N, 5.34. Found: N, 5.33 and 5.32.

2,7-Diaminodibenzofuran. (A) From 2-Bromo-7-aminodibenzofuran.—One-half gram of 2-bromo-7-aminodibenzofuran was heated in a sealed tube at 205° for seventeen hours with 1 g. of cuprous bromide and 20 cc. of ammonium hydroxide. The yield of 2,7-diaminodibenzofuran was 27%, and the compound was shown to be identical (mixed m. p.) with a specimen prepared by Cullinane's method by the reduction of 2,7-dinitrodibenzofuran.[17]

(B) From 2-Amino-7-nitrodibenzofuran.—One and one-half grams of 2-bromo-7-nitrodibenzofuran was heated in a sealed tube with 1 g. of cuprous chloride and 25 cc. of ammonium hydroxide at 208–210° for ten hours and then at 150–160° for five hours. The 2-amino-7-nitrodibenzofuran was obtained in 10.8% yield, and separated from an alcoholic ammonium hydroxide solution as small, brown glistening plates melting at 143°. Reduction of the nitro-amine by tin and hydrochloric acid gave 2,7-diaminodibenzofuran.

Conversion of 2-Bromo-7-nitrodibenzofuran to 2,7-Dibromodibenzofuran.—Five grams of 2-bromo-7-nitrodibenzofuran was reduced in the usual manner by tin and concd. hydrochloric acid. An ether–benzene extract of the reaction product yielded 0.4 g. of unchanged bromonitro compound. One gram of the bromo-amine was diazotized and the diazo solution treated with cuprous bromide and hydrobromic acid to yield 2,7-dibromodibenzofuran. Identification was completed by comparison with an authentic specimen kindly provided by Professor McCombie.

2-Bromo-3-nitrodibenzofuran.—Concentration of the benzene mother liquors resulting from extraction of the nitration product of 2-bromodibenzofuran gave 10.5 g. of yellow plates melting between 138–148°. One crystallization from a small volume of benzene sufficed to give pure 2-bromo-3-nitrodibenzofuran melting at 154.5–155.5°. The yield of pure compound was 4.8 g. or 8.2%.

Anal. Calcd. for $C_{12}H_6O_3NBr$: N, 4.79. Found: N, 4.88 and 5.06.

Further evaporation of the benzene solution gave 6 g. of an oily red material melting between 109–125°. This was not further investigated, but it indicates the possibility of another isomer.

Reduction of 2-Bromo-3-nitrodibenzofuran.—One gram of the bromonitro compound was reduced by tin and hydrochloric acid to 2-bromo-3-aminodibenzofuran hydrochloride. The 2-bromo-3-aminodibenzofuran, liberated by treating the hydrochloride with ammonium hydroxide, melted at 127–128° and was shown to be identical with the bromo-amine obtained by bromination of 3-diacetaminodibenzofuran.

It is significant that in the nitration of 2-bromodibenzofuran the nitro group assumes a position equivalent to that involved when no substituent is present. This relative independence of the two benzo nuclei is reflected in the nitration of tetrahydrodibenzofuran. Mr. E. W. Smith has shown that the nitro group goes to the 3-position in the non-reduced cycle.

Nitration of 3-Bromodibenzofuran.—In extension of the problem of the orienting influence of typical monosubstituted dibenzofurans, 12.4 g. (0.05 mole) of 3-bromodibenzofuran (prepared from 3-aminodibenzofuran by means of the diazo reaction) was nitrated by an acetic acid solution of nitric acid (sp. gr., 1.5). Crystallization of the reaction product from chloroform gave a 34% yield of fine yellow needles melting at 251°. The structure of this bromonitro compound has not yet been established, but it probably is 3-bromo-7-nitrodibenzofuran.

Anal. Calcd. for $C_{12}H_6O_3NBr$: N, 4.79. Found: N, 4.70 and 4.66.

The bromo-nitro compound (2.2 g.) was aminated by heating in a sealed tube at 200° for twenty-two hours with 3 g. of cuprous bromide and 25 cc. of ammonium hydroxide. The yield of nitro-amine (probably 3-amino-7-nitrodibenzofuran) melting at 133° after crystallization from aqueous alcohol was 21%.

Anal. Calcd. for $C_{12}H_8O_3N_2$: N, 12.28. Found: N, 12.67.

The authors are grateful to Dr. A. W. Dox for suggestions.

Summary

Homonuclear substitution occurs with 2-amino- and 3-aminodibenzofuran, the second substituent entering the 3- and 2-positions, respectively. In dichlorination and di-iodination, heteronuclear substitution takes place with the formation of 2,8-dihalogenodibenzofurans. Nitration of 2-bromodibenzofuran gives both homo- and heteronuclear substitution products: namely, 2-bromo-3-nitro dibenzofuran and 2-bromo-7-nitrodibenzofuran.

The possibilities of preliminary mercuration and nitration during iodination by means of mercuric oxide and nitric acid, respectively, are excluded in the case of dibenzofuran.

AMES, IOWA RECEIVED AUGUST 13, 1934

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[17] Cullinane, *J. Chem. Soc.*, 2366 (1932).